

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date
16 December 2004 (16.12.2004)

PCT

(10) International Publication Number
WO 2004/108875 A1

(51) International Patent Classification⁷: C11D 10/04, 3/20, 3/36, 3/06, 3/02

(74) Agent: BROWN, Andrew Stephen; Reckitt Benckiser plc, Group Patents Department, Dansom Lane, Hull, HU8 7DS (GB).

(21) International Application Number:

PCT/GB2004/002180

(22) International Filing Date: 19 May 2004 (19.05.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0313158.8 7 June 2003 (07.06.2003) GB

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(71) Applicant (for all designated States except MN, US): RECKITT BENCKISER INC [US/US]; Morris Corporate Center IV, 399 Interpace Parkway, Parsippany, NJ 07054 (US).

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (for MN only): RECKITT BECKISER (UK) LIMITED [GB/GB]; 103-105 Bath Road, Slough, Berkshire SL1 3UH (GB).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations
- of inventorship (Rule 4.17(iv)) for US only

Published:

- with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/108875 A1

(54) Title: HARD SURFACE CLEANING COMPOSITIONS CONTAINING SOAPS

(57) Abstract: Aqueous hard surface cleaning compositions based on Marseilles soaps further comprise a surfactant constituent, desirably an anionic surfactant, a nonionic surfactant or mixtures thereof, a source of potassium ions and optionally one or more of: an organic solvent constituent, especially one or more glycol ethers, a preservative constituent, and one or more further constituents which are directed to improving the aesthetic or functional features of the inventive compositions. The compositions demonstrate excellent storage stability at elevated temperatures, at room temperature and following successive freeze-thaw cycles.

HARD SURFACE CLEANING COMPOSITIONS CONTAINING SOAPS

5 The present invention relates to hard surface cleaning compositions which include soaps. More specifically the present application relates to hard surface cleaning compositions based on potassium salt containing soaps.

Soaps are amongst the oldest known cleaning agents. Soaps are generally produced by combining fats or oils with alkalis or alkaline earths, usually by boiling, and 10 consists of various salts e.g., potassium, sodium, of various fatty acids, e.g., oleic, stearic, palmitic, etc. According to this general reaction, many different soaps may be produced by variation of the reactants, especially the source of fats and/or oils which are reacted alkalis or alkaline earth. One well known type of soap is "Marseilles" soap, which is often generally formed by the reaction of a substantial proportion of olive oil with alkalis 15 or alkaline earths, or with one or more naturally occurring sources of alkali materials such as seawater, with the resultant soap being a fine-grained hard soap, having either a white or mottled appearance, or may also be a liquid at room temperature.

Cleaning compositions which may also provide a disinfecting or sanitizing effect are commercially important products. Such are typically aqueous compositions which 20 typically include one or more synthetic surfactants and one or more organic solvents which in conjunction with the water present provide a primary cleaning benefit to a treated surface, such as a stained hard surface. Optionally such cleaning compositions may also include a disinfecting effective or sanitizing effective agent which acts to provide a simultaneous disinfecting benefit with the cleaning benefit provided to a hard 25 surface as well. Rarely however do such cleaning compositions include any appreciable amounts of soap as on the one hand the one or more synthetic surfactants typically widely and inexpensively available and are effective, while on the other hand it is known that the incorporation of soaps into a cleaning composition is rarely a trivial exercise in chemical formulation. Nonetheless it would be desirable to provide a cleaning composition, 30 particularly a liquid cleaning composition which includes a significant amount of a soap, particularly a soap which is produced from natural sources of fats and oils.

According to the one aspect of the invention, there is provided an aqueous hard surface cleaning composition which comprises (preferably consists essentially of):

- 5 Marseilles soap;
- a surfactant constituent, desirably an anionic surfactant, a nonionic surfactant or mixtures thereof, but most desirably solely a nonionic surfactant;
- 10 a source of potassium ions;
- optionally but desirably an organic solvent constituent, desirably one or more glycol ethers;
- optionally but desirably a preservative constituent;
- 15 optionally one or more further constituents which are directed to improving the aesthetic or functional features of the inventive compositions;
- the balance being water.

In further aspects of the invention there are provided processes for the production of the aforesaid compositions.

- 15 Particularly preferred compositions exhibit good stability upon storage, at room temperature, at elevated temperatures, and after successive freeze-thaw cycles.

It is yet a further object of the invention to provide a cleaning composition which features the benefits described above.

- 20 It is a further object of the invention to provide a process for the cleaning of hard surfaces, which process comprises the step of: providing a composition as outlined above, and applying an effective amount to a hard surface requiring such treatment.

A still further object of the invention is directed to a process for the manufacture a cleaning composition described above.

- 25 The compositions of the invention include a soap constituent, particularly a soap constituent based on sodium soaps. A particularly preferred soap is marketed as "Marseilles" soap which is broadly described to be a composition based on the sodium salts of fatty acids derived from olive oil and/or cottonseed oils. Generally Marseilles soap is described to be a mixture of olive oils and vegetable oils (copra oils, palm oils) which are reacted with alkaline ash derived from sea vegetation as well as with saline water obtained from the Mediterranean Sea. The specific composition of such Marseilles soap may vary slightly amongst manufacturers however the sale of this product is

regulated to comprise at least 72%wt. pure soap, and to contain not more than 0.1%wt. free soda, not more than 0.4%wt. sodium chloride, and to contain not more than 0.5%wt. glycerol. Little or no coloring or artificial additives are included in the product. A traditional process for manufacturing Marseilles soap is described to include the

5 following steps: the mixture of olive oils and vegetable oils is provided with the alkalis or alkaline earths (soda) to permit saponification of the oils, and this mixture is then cooked at about 120°C for about 10 days; subsequently the mixture is washed with seawater in order to remove the soda used in the saponification reaction, and the resultant composition is permitted to lay undisturbed for about 2 days; optionally one or more
10 further wash operations, usually with fresh water (non-saline) may be used to further rinse any remaining alkali from the soap mixture; and, finally the mixture at an elevated temperature (usually 50°C - 70°C) is poured into forms in which it is allowed to cool and dry, after which it may be removed.

15 The Marseilles soap is present in the aqueous hard surface cleaning compositions of the present invention in an amount of from about 0.2%wt. to about 3.0% by weight, more preferably is present in an amount of from about 0.55 – 1.75%wt., and most preferably is present in an amount of from about 0.85 -1.5%wt.

The inventive compositions further necessarily include a surfactant constituent, which is desirably an anionic surfactant, a nonionic surfactant, or mixtures thereof

20 Generally any nonionic surfactant material may be used in the inventive compositions. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with an alkylene oxide, especially ethylene oxide or with the polyhydration product thereof, a polyalkylene glycol, especially polyethylene glycol, to form a water soluble or
25 water dispersible nonionic surfactant compound. By way of non-limiting example, particularly examples of suitable nonionic surfactants which may be used in the present invention include the following:

30 One class of useful nonionic surfactants includes polyalkylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with an alkylene oxide, especially an ethylene

oxide, the ethylene oxide being present in an amount equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds can be derived, for example, from polymerized propylene, diisobutylene and the like. Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol; dodecylphenol condensed with about 12 moles of ethylene oxide per mole of phenol; dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol and diisoctyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol.

A further class of useful nonionic surfactants includes the condensation products of aliphatic alcohols with from about 1 to about 60 moles of an alkylene oxide, especially an ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of alcohol and the condensation product of about 9 moles of ethylene oxide with coconut alcohol (a mixture of fatty alcohols with alkyl chains varying in length from about 10 to 14 carbon atoms). Other examples are those C₆ -C₁₁ straight-chain alcohols which are ethoxylated with from about 3 to about 6 moles of ethylene oxide. Their derivation is well known in the art. Examples include Alfonic® 810-4.5, which is described in product literature from Sasol as a C₈-C₁₀ straight-chain alcohol having an average molecular weight of 356, an ethylene oxide content of about 4.85 moles (about 60 wt.%), and an HLB of about 12; Alfonic® 810-2, which is described in product literature as a C₈-C₁₀ straight-chain alcohols having an average molecular weight of 242, an ethylene oxide content of about 2.1 moles (about 40 wt.%), and an HLB of about 12; and Alfonic® 610-3.5, which is described in product literature as having an average molecular weight of 276, an ethylene oxide content of about 3.1 moles (about 50 wt.%), and an HLB of 10. Other examples of alcohol ethoxylates are C₁₀ oxo-alcohol ethoxylates available from BASF under the Lutensol® ON tradename. They are available in grades containing from about 3 to about 11 moles of ethylene oxide (available under the names Lutensol® ON 30; Lutensol® ON 50; Lutensol® ON 60; Lutensol® ON 65; Lutensol® ON 66; Lutensol® ON 70; Lutensol® ON 80; and Lutensol® ON 110). Other examples of ethoxylated alcohols

include the Neodol® 91 series non-ionic surfactants available from Shell Chemical Company which are described as C₉-C₁₁ ethoxylated alcohols. The Neodol® 91 series non-ionic surfactants of interest include Neodol® 91-2.5, Neodol® 91-6, and Neodol® 91-8. Neodol® 91-2.5 has been described as having about 2.5 ethoxy groups per molecule; Neodol 91-6 has been described as having about 6 ethoxy groups per molecule; and Neodol 91-8 has been described as having about 8 ethoxy groups per molecule.

Further examples of ethoxylated alcohols include the Rhodasurf® DA series non-ionic surfactants available from Rhodia which are described to be branched isodecyl alcohol ethoxylates. Rhodasurf® DA-530 has been described as having 4 moles of ethoxylation and an HLB of 10.5; Rhodasurf® DA-630 has been described as having 6 moles of ethoxylation with an HLB of 12.5; and Rhodasurf® DA-639 is a 90% solution of DA-630. Further examples of ethoxylated alcohols include those from Tomah Products (Milton, WI) under the Tomadol® tradename with the formula RO(CH₂CH₂O)_nH where R is the primary linear alcohol and n is the total number of moles of ethylene oxide. The ethoxylated alcohol series from Tomah include 91-2.5; 91-6; 91-8 - where R is linear C₉/C₁₀/C₁₁ and n is 2.5, 6, or 8; 1-3; 1-5; 1-7; 1-73B; 1-9; where R is linear C₁₁ and n is 3, 5, 7 or 9; 23-1; 23-3; 23-5; 23-6.5 - where R is linear C₁₂/C₁₃ and n is 1, 3, 5, or 6.5; 25-3; 25-7; 25-9; 25-12 - where R is linear C₁₂/C₁₃/C₁₄/ C₁₅ and n is 3, 7, 9, or 12; and 45-7; 45-13 - where R is linear C₁₄/ C₁₅ and n is 7 or 13.

A further class of useful nonionic surfactants include primary and secondary linear and branched alcohol ethoxylates, such as those based on C₆-C₁₈ alcohols which further include an average of from 2 to 80 moles of ethoxylation per mol of alcohol. These examples include the Genapol® UD (ex. Clariant, Muttenz, Switzerland) described under the tradenames Genapol® UD 030, C₁₁-oxo-alcohol polyglycol ether with 3 EO; Genapol® UD, 050 C₁₁-oxo-alcohol polyglycol ether with 5 EO; Genapol® UD 070, C₁₁-oxo-alcohol polyglycol ether with 7 EO; Genapol® UD 080, C₁₁-oxo-alcohol polyglycol ether with 8 EO; Genapol® UD 088, C₁₁-oxo-alcohol polyglycol ether with 8 EO; and Genapol® UD 110, C₁₁-oxo-alcohol polyglycol ether with 11 EO.

A further class of useful nonionic surfactants includes those surfactants having a formula:



wherein;

R is a mixture of linear, even carbon-number hydrocarbon chains ranging from C₁₂H₂₅ to C₁₆H₃₃ and n represents the number of ethoxy repeating units and is a number of from about 1 to about 12.

5 Surfactants of this formula are presently marketed under the Genapol® tradename (ex. Clariant), which surfactants include the "26-L" series of the general formula RO(CH₂CH₂O)_nH wherein R is a mixture of linear, even carbon-number hydrocarbon chains ranging from C₁₂H₂₅ to C₁₆H₃₃ and n represents the number of repeating units and is a number of from 1 to about 12, such as 26-L-1, 26-L-1.6, 26-L-2, 26-L-3, 26-L-5, 26-
10 L-45, 26-L-50, 26-L-60, 26-L-60N, 26-L-75, 26-L-80, 26-L-98N, and the 24-L series, derived from synthetic sources and typically contain about 55% C₁₂ and 45% C₁₄ alcohols, such as 24-L-3, 24-L-45, 24-L-50, 24-L-60, 24-L-60N, 24-L-75, 24-L-92, and 24-L-98N, all sold under the Genapol® tradename.

15 A further class of useful nonionic surfactants include alkoxy block copolymers, and in particular, compounds based on ethoxy/propoxy block copolymers. Polymeric alkylene oxide block copolymers include nonionic surfactants in which the major portion of the molecule is made up of block polymeric C₂-C₄ alkylene oxides. Such nonionic surfactants, while preferably built up from an alkylene oxide chain starting group, and can have as a starting nucleus almost any active hydrogen containing group including, 20 without limitation, amides, phenols, thiols and secondary alcohols.

One group of such useful nonionic surfactants containing the characteristic alkylene oxide blocks are those which may be generally represented by the formula (A):



25 where EO represents ethylene oxide,
PO represents propylene oxide,
y equals at least 15,
(EO)_{x+y} equals 20 to 50% of the total weight of said compounds, and, the
30 total molecular weight is preferably in the range of about 2000 to 15,000. These surfactants are available under the PLURONIC (ex. BASF) or Emulgen (ex. Kao.)

A further group of such useful nonionic surfactants containing the characteristic alkylene oxide blocks are those can be represented by the formula (B):



5

wherein R is an alkyl, aryl or aralkyl group, where the R group contains 1 to 20 carbon atoms, the weight percent of EO is within the range of 0 to 45% in one of the blocks a, b, and within the range of 60 to 100% in the other of the blocks a, b, and the total number of moles of combined EO and PO is in the range of 6 to 125 moles, with 1 to 50 moles in the PO rich block and 5 to 100 moles in the EO rich block. Specific nonionic surfactants which in general are encompassed by Formula B include butoxy derivatives of propylene oxide/ethylene oxide block polymers having molecular weights within the range of about 2000-5000.

10 Still further examples of useful nonionic surfactants include those which can be represented by formula (C) as follows:



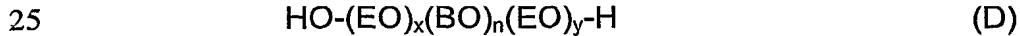
wherein EO represents ethylene oxide,

BO represents butylene oxide,

20 R is an alkyl group containing 1 to 20 carbon atoms,

n is about 5-15 and x is about 5-15.

Yet further useful nonionic surfactants include those which may be represented by the following formula (D):



wherein EO represents ethylene oxide,

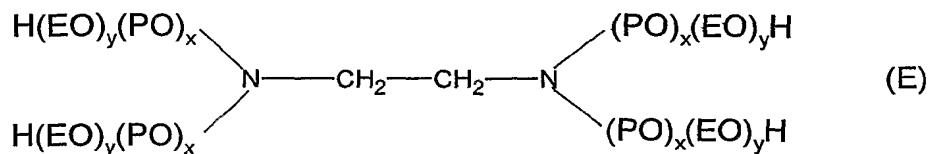
BO represents butylene oxide,

30 n is about 5-15, preferably about 15,

x is about 5-15, preferably about 15, and

y is about 5-15, preferably about 15.

Still further exemplary useful nonionic block copolymer surfactants include ethoxylated derivatives of propoxylated ethylene diamine, which may be represented by the following formula:



5

where (EO) represents ethoxy,
(PO) represents propoxy,

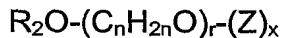
the amount of $(PO)_x$ is such as to provide a molecular weight prior to ethoxylation of about 300 to 7500, and the amount of $(EO)_y$ is such as to provide about 20% to 90% of the total weight of said compound.

Further useful non-ionic surfactants which may be used in the inventive compositions include those presently marketed under the trade name Pluronics® (ex. BASF). The compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion of the molecule is of the order of 950 to 4,000 and preferably 200 to 2,500. The addition of polyoxyethylene radicals of the hydrophobic portion tends to increase the solubility of the molecule as a whole so as to make the surfactant water-soluble. The molecular weight of the block polymers varies from 1,000 to 15,000 and the polyethylene oxide content may comprise 20% to 80% by weight. Preferably, these surfactants are in liquid form and particularly satisfactory surfactants are available as those marketed as Pluronics® L62 and Pluronics® L64.

Alkylmonoglycosides and alkylpolyglycosides which find use in the present inventive compositions include known nonionic surfactants which are alkaline and electrolyte stable. Alkylmonoglycosides and alkylpolyglycosides are prepared generally by reacting a monosaccharide, or a compound hydrolyzable to a monosaccharide with an alcohol such as a fatty alcohol in an acid medium. Various glycoside and polyglycoside

compounds including alkoxylated glycosides and processes for making them are disclosed in U.S. Pat. Nos. 2,974,134; 3,219,656; 3,598,865; 3,640,998; 3,707,535, 3,772,269; 3,839,318; 3,974,138; 4,223,129 and 4,528,106 the contents of which are incorporated by reference.

5 One exemplary group of such useful alkylpolyglycosides includes those according to the formula:



wherein:

10 R_2 is a hydrophobic group selected from alkyl groups, alkylphenyl groups, hydroxyalkylphenyl groups as well as mixtures thereof, wherein the alkyl groups may be straight chained or branched, and which contain from about 8 to about 18 carbon atoms, n has a value of 2 – 8, especially a value of 2 or 3;

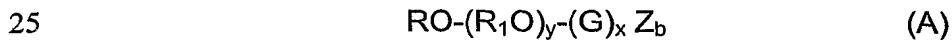
15 r is an integer from 0 to 10, but is preferably 0,

Z is derived from glucose; and,

x is a value from about 1 to 8, preferably from about 1.5 to 5.

Preferably the alkylpolyglycosides are nonionic fatty alkylpolyglucosides which contain a straight chain or branched chain $C_8 - C_{15}$ alkyl group, and have an average of from about 1 to 5 glucose units per fatty alkylpolyglucoside molecule. More preferably, the nonionic fatty alkylpolyglucosides which contain straight chain or branched $C_8 - C_{15}$ alkyl group, and have an average of from about 1 to about 2 glucose units per fatty alkylpolyglucoside molecule.

A further exemplary group of alkyl glycoside surfactants suitable for use in the practice of this invention may be presented by the following formula (A):



wherein:

R is a monovalent organic radical containing from about 6 to about 30, preferably from about 8 to 18 carbon atoms,

R_1 is a divalent hydrocarbon radical containing from about 2 to about 4 carbon atoms,

30 y is a number which has an average value from about 0 to about 1 and is preferably 0,

G is a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms; and,

x is a number having an average value from about 1 to 5 (preferably from 1.1 to 2);

Z is O_2M^1 , $—O—C(=O)—R_2$, $O(CH_2)$, CO_2M^1 , OSO_3M^1 , or $O(CH_2)SO_3M^1$; R_2 is $(CH_2)CO_2M^1$ or $CH=CHCO_2M^1$; (with the proviso that Z can be O_2M^1 only if Z is in place of a primary hydroxyl group in which the primary hydroxyl-bearing carbon atom, --

5 CH₂OH, is oxidized to form a $—C(=O)—OM^1$ group)

b is a number of from 0 to $3x+1$ preferably an average of from 0.5 to 2 per glycosal group;

p is 1 to 10, M^1 is H^+ or an organic or inorganic counterion, particularly cations such as, for example, an alkali metal cation, ammonium cation, monoethanolamine cation or 10 calcium cation. As defined in Formula (A) above, R is generally the residue of a fatty alcohol having from about 8 to 30 and preferably 8 to 18 carbon atoms. Examples of such alkylglycosides as described above include, for example APG 325 CS Glycoside® which is described as being a 50% C₉ -C₁₁ alkyl polyglycoside, also commonly referred to as D-glucopyranoside, (commercially available from Henkel KGaA) and Glucopon® 625 CS 15 which is described as being a 50% C₁₀ -C₁₆ alkyl polyglycoside, also commonly referred to as a D-glucopyranoside, (ex. Henkel).

Further nonionic surfactants which may be included in the inventive compositions include alkoxylated alkanolamides, preferably C₈-C₂₄ alkyl di(C₂-C₃ alkanol amides), as represented by the following formula:



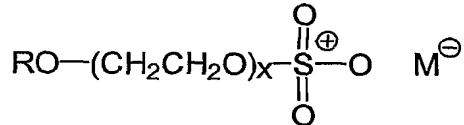
wherein R_5 is a branched or straight chain C₈-C₂₄ alkyl radical, preferably a C₁₀-C₁₆ alkyl radical and more preferably a C₁₂-C₁₄ alkyl radical, and R_6 is a C₁-C₄ alkyl radical, preferably an ethyl radical.

According to certain particularly preferred embodiments the surfactant constituent 25 comprises a nonionic surfactant based on a linear primary alcohol ethoxylate particularly wherein the alkyl portion is a C₈ to C₁₂, but particularly a C₉ to C₁₁ alkyl group, and having an average of between about 6 to about 8 moles of ethoxylation.

Further, in certain preferred embodiments on the invention, the surfactant constituent consists solely of one or more nonionic surfactants to the exclusion of anionic or other classes of surfactants. Very desirably, the sole surfactant present is a linear primary alcohol ethoxylate, especially the linear primary alcohol ethoxylate noted above.

5 Generally any anionic surfactant material may be used in the inventive compositions. By way of non-limiting example, particularly suitable anionic surfactants include: alkali metal salts, ammonium salts, amine salts, or aminoalcohol salts of one or more of the following compounds (linear and secondary): alcohol sulfates and sulfonates, alcohol phosphates and phosphonates, alkyl sulfates, alkyl ether sulfates, sulfate esters of an alkylphenoxy polyoxyethylene ethanol, alkyl monoglyceride sulfates, alkyl sulfonates, olefin sulfonates, paraffin sulfonates, beta-alkoxy alkane sulfonates, alkylamidoether sulfates, alkylaryl polyether sulfates, monoglyceride sulfates, alkyl ether sulfonates, ethoxylated alkyl sulfonates, alkylaryl sulfonates, alkyl benzene sulfonates, alkylamide sulfonates, alkyl monoglyceride sulfonates, alkyl carboxylates, alkyl sulfoacetates, alkyl ether carboxylates, alkyl alkoxy carboxylates having 1 to 5 moles of ethylene oxide, alkyl sulfosuccinates, alkyl ether sulfosuccinates, alkylamide sulfosuccinates, alkyl sulfosuccinamates, octoxynol or nonoxynol phosphates, alkyl phosphates, alkyl ether phosphates, taurates, N-acyl taurates, fatty taurides, fatty acid amide polyoxyethylene sulfates, isethionates, acyl isethionates, and sarcosinates, acyl 10 sarcosinates, or mixtures thereof. Generally, the alkyl or acyl radical in these various compounds comprise a carbon chain containing 12 to 20 carbon atoms.

15 Exemplary anionic surfactants useful in forming the compositions of the invention include alkyl sulfates which may be represented by the following general formula:

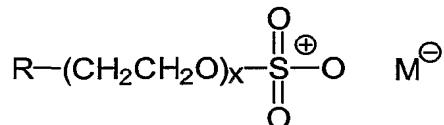


20 25 wherein R is an straight chain or branched alkyl chain having from about 8 to about 18 carbon atoms, saturated or unsaturated, and the longest linear portion of the alkyl chain is 15 carbon atoms or less on the average, M is a cation which makes the compound water soluble especially an alkali metal such as sodium, or is ammonium or substituted

ammonium cation, and x is from 0 to about 4. Of these, most preferred are the non-ethoxylated C₁₂-C₁₅ primary and secondary alkyl sulfates.

Exemplary commercially available alkyl sulfates include one or more of those available under the tradenames RHODAPON® (ex. Rhône-Poulenc Co.) as well as STEPANOL® (ex. Stepan Chemical Co.). Exemplary alkyl sulfates which is preferred for use is a sodium lauryl sulfate surfactant presently commercially available as RHODAPON® LCP (ex. Rhône-Poulenc Co.), as well as a further sodium lauryl sulfate surfactant composition which is presently commercially available as STEPANOL® WAC (ex. Stepan Chemical Co.).

Further exemplary anionic surfactants useful in forming the compositions of the invention include alkyl sulfonate anionic surfactants which may be represented according to the following general formula:



wherein R is an straight chain or branched alkyl chain having from about 8 to about 18 carbon atoms, saturated or unsaturated, and the longest linear portion of the alkyl chain is 15 carbon atoms or less on the average, M is a cation which makes the compound water soluble especially an alkali metal such as sodium, or is ammonium or substituted ammonium cation, and x is from 0 to about 4. Most preferred are the C₁₂-C₁₅ primary and secondary alkyl sulfates.

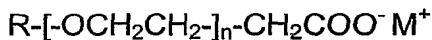
Exemplary, commercially available alkane sulfonate surfactants include one or more of those available under the tradename HOSTAPUR® (ex. Clariant).

According to certain particularly preferred embodiments the surfactant constituent comprises an anionic surfactant based on alkylbenzene sulfonates. Desirably these alkylbenzene sulfonates comprise an alkyl group containing from about 9 to about 15 carbon atoms, in a straight chain or in a branched chain. Particularly useful are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 14.

Also contemplated to be useful as anionic surfactants are carboxylates which include alkyl- and alkylaryl-carboxylates which include those which may be represented by the general formula:



5 wherein R is a straight or branched hydrocarbon chain containing from about 9 to 21 carbon atoms, and which may also include an aromatic ring, especially a phenyl group as part of the hydrocarbon chain, and M is a metal or ammonium ion. Further preferred alkylpolyoxycarboxylates include polyethoxycarboxylates which may be represented by the general formula:



10 wherein R is a straight chained or branched hydrocarbon chain which may include an aryl moiety, but is desirably a straight chained or branched hydrocarbon chain; and n is an integer value of from 1 – 24, and M is a metal or ammonium ion, but is preferably a alkali or alkaline earth metal ion, especially sodium.

15 Exemplary useful alkylpolyoxycarboxylates and alkylarylpolycarboxylates include those commercially available in the SANDOPAN series from Clariant Inc. (Charlotte, NC), as well as in the SURFINE series from Finetex, Inc.

20 Further, in certain preferred embodiments on the invention, the surfactant constituent consists of a linear primary alcohol ethoxylate with one or more linear straight chain alkylbenzene sulfonates, but may alternately consists solely of one or more anionic surfactants to the exclusion of nonionic or other classes of surfactants.

25 The surfactant constituent is present in the compositions of the present invention in an amount of from about 0.01%wt. to about 50%wt., more preferably is present in an amount of from 0.01 – 10%wt. Although the surfactant constituent may comprise one or more surfactants based on anionic, nonionic or both anionic and nonionic surfactants according to certain preferred embodiments the surfactant constituent consists exclusively of one or more nonionic surfactants, particularly solely a linear primary alcohol ethoxylate.

30 The inventive compositions optionally but very desirably comprise at least one organic solvent constituent, which may be one or more alcohols, glycols, acetates, ether acetates and glycol ethers. Exemplary alcohols useful in the compositions of the

invention include C₁-C₈ alcohols which may be straight chained or branched, and which are specifically intended to include both primary and secondary alcohols. Exemplary glycol ethers include those glycol ethers having the general structure R_a-O-R_b-OH, wherein R_a is an alkoxy of 1 to 20 carbon atoms, or aryloxy of at least 6 carbon atoms,

5 and R_b is an ether condensate of propylene glycol and/or ethylene glycol having from one to ten glycol monomer units. Preferred are glycol ethers having one to five glycol monomer units. These are C₃-C₂₀ glycol ethers. By way of further non-limiting example specific useful organics solvents include propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol n-propyl ether,

10 ethylene glycol n-butyl ether, diethylene glycol n-butyl ether, diethylene glycol methyl ether, propylene glycol, ethylene glycol, isopropanol, ethanol, methanol, diethylene glycol monoethyl ether acetate and particularly advantageously ethylene glycol hexyl ether, diethylene glycol hexyl ether, as well as the C₃-C₈ primary and secondary alcohols, especially isopropyl alcohol. Exemplarily useful organic solvents include those presently

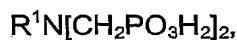
15 commercially available under the tradenames Carbitol®, and Cellosolve® (Union Carbide Div. of Dow Chemical., Danbury CT), Dowanol® (Dow Chemical Co., Midland MI) and Arcosolv® (ARCO Chemical Co., Newton Square PA). Particularly useful are those organic solvents which are illustrated in the Examples. Particularly preferred are one or more of: dipropylene glycol n-butyl ether, propylene glycol n-butyl ether, ethylene

20 glycol butyl ether, diethylene glycol butyl ether, propylene glycol n-propyl ether, and propylene glycol methyl ether. In certain specific embodiments the organic solvent constituent comprises one or more glycol ethers and optionally one or more alcohols, but preferably the sole organic solvent present in the compositions are one or more glycol ethers.

25 The organic solvent constituent is present in the compositions of the present invention in an amount of from about 0.01%wt. to about 20%wt., more preferably is present in an amount of from about 0.01 - 15%wt., and most preferably is present in an amount of from about 0.01 – 10%wt.

The compositions of the invention also necessarily include a source of potassium ions. Materials for use as a source of potassium ions include inorganic potassium salts of any form which are soluble or dispersible in water and which make available potassium

ions to the aqueous composition. Exemplary useful phosphates include alkali metal pyrophosphate, an alkali metal polyphosphate such as potassium tripolyphosphate. Exemplary useful phosphonic acids include, mono-, di-, tri- as well as tetra-phosphonic acids which may optionally also contain other functional groups such as carboxy, 5 hydroxyl, thio and the like. Among these are phosphonic acids which may be represented by one of the following general formula:



wherein R^1 may represent a $-(C_1-C_6\text{alkylene})-N-[CH_2PO_3H_2]_2$ group or may represent a third $-(CH_2PO_2H_2)$ group,

10 or,



wherein R^2 is a C_1-C_6 alkyl group.

15 The phosphonic acid may also comprise potassium salts of a low molecular weight phosphonopolycarboxylic acid such as one having about 2 – 4 carboxylic acid moieties and about 1 – 3 phosphonic acid groups, as well as potassium salts of alkylene phosphonic acids such as methylene phosphonic acids, and phosphorous acid (H_3PO_3) as well.

Preferred materials for use as a source of potassium ions include potassium carbonates, potassium phosphates, potassium polyphosphates, and potassium 20 pyrophosphates. Particularly preferred are potassium tripolyphosphate, tetrapotassium pyrophosphate and potassium hydroxide of which tetrapotassium pyrophosphate is particularly preferred.

Advantageously any material or materials which functions as the source of potassium ions is present in sufficient amounts such that the final concentration of 25 available potassium ions in the inventive compositions are from about $1 \cdot 10^{14}$ to about $1 \cdot 10^{18}$, but preferably from about $1 \cdot 10^{16}$ to about $1 \cdot 10^{18}$, and most preferably from about $1 \cdot 10^{17}$ to about $5 \cdot 10^{17}$ potassium ions per liter of composition. In the alternative the source of potassium ions is present in sufficient amounts such that the final concentration 30 of available potassium ions in the inventive compositions are from about 50 ppm to about 20,000 ppm, but preferably the available potassium ions are present in the inventive compositions in amounts of from about 2000 ppm to about 6000 ppm.

The present inventors have surprisingly found that compositions exhibiting good stability can be achieved wherein there is a sufficient concentration of available potassium ions in the aqueous compositions. While not wishing to be bound by the following, it is hypothesized that the potassium ions substitute a significant proportion of the sodium salts of the C₁₄, C₁₆, C₁₈ and C₂₀ fatty acids present in the soap constituent, especially in Marseilles soap, forming potassium salts of these fatty acids which exhibit improved aqueous solubility. The raw materials used to produce Marseilles soap is rich in such C₁₄, C₁₆, C₁₈ and C₂₀ fatty acids. Surprisingly the inventors have found that this improved aqueous solubility has a striking effect on the stability of the inventive compositions as evidenced by the behavior of the inventive compositions when subjected to storage at both room temperature, storage under elevated temperatures (105°F, 120°F) and to successive freeze-thaw cycles.

Advantageously the compositions according to the present invention comprise a preservative constituent. Since a significant portion of the formulation comprises water, it is preferably that the preservative be water soluble. Desirably, the selected water soluble preservatives are those which exhibit stability and efficacy in the aqueous compositions according to the invention at neutral, but preferably at alkaline pH's especially in the preferred pH ranges noted above. Such water soluble preservatives include compositions which include parabens, including methyl parabens and ethyl parabens, glutaraldehyde, formaldehyde, 2-bromo-2-nitropropoane-1,3-diol, 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazoline-3-one, and mixtures thereof. One exemplary composition is a combination 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one where the amount of either component may be present in the mixture anywhere from 0.001 to 99.99 weight percent, based on the total amount of the preservative. For reasons of availability, the most preferred preservative are those commercially available preservative comprising a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one marketed under the trademark KATHON® CG/ICP as a preservative composition presently commercially available from Rohm and Haas (Philadelphia, PA). Further useful preservative compositions include KATHON® CG/ICP II, a further preservative composition presently commercially available from Rohm and Haas (Philadelphia, PA), PROXEL® which is presently commercially

available from Zeneca Biocides (Wilmington, DE), SUTTOCIDE® A which is presently commercially available from Sutton Laboratories (Chatam, NJ) as well as TEXTAMER® 38AD which is presently commercially available from Calgon Corp. (Pittsburgh, PA).

Particularly preferred for use in the inventive composition is a preparation containing 1,3-
5 dihydroxymethyl-5,5-dimethylhydantoin and 3-iodo-2-propynyl butyl carbamate which is presently commercially available as Dantogard® Plus Liquid from Lonza Corp.

(Fairlawn, NJ.)

When included, the preservative constituent is present in the compositions of the present invention in any amount which is effective in retarding or eliminating the growth
10 of undesired microorganisms in the inventive compositions particularly upon standing.

The preservative constituent need be present in only minor amounts, and is advantageously present in amounts for from about 0.1%wt. to about 0.8%wt., more preferably is present in an amount of from about 0.2 – 0.6%wt. In preferred
embodiments of the invention the preservative constituent is necessarily present.

15 The compositions of the present invention may also optionally comprise one or more further optional constituents which are directed to improving the aesthetic or functional features of the inventive compositions. By way of non-limiting example such further constituents include one or more of: coloring agents, fragrances and fragrance solubilizers, viscosity modifying agents, other surfactants, pH adjusting agents and pH

20 buffers including organic and inorganic salts, optical brighteners, opacifying agents, hydrotropes, antifoaming agents, enzymes, and anti-oxidants. When one or more of the optional constituents is added, i.e., fragrance and/or coloring agents, the esthetic and consumer appeal of the product is often favorably improved. The use and selection of these optional constituents is well known to those of ordinary skill in the art and any
25 optional constituent may be included which does not deleteriously effect the favorable properties of the invention.

While not an essential feature in all embodiments of the inventive compositions, according to certain preferred embodiments the liquid compositions of the invention necessarily comprise at least one fragrancing agent. Such may be one or more substances
30 or mixtures of substances including those which are naturally derived (i.e., obtained by extraction of flower, herb, blossom or plant), those which are artificially derived or

produced (i.e., mixture of natural oils and/or oil constituents), and those which are synthetically produced substances (odiferous substances). In the present invention, the precise composition of the fragrance constituent is of no particular consequence as long as it may be effectively included as a constituent of the compositions, and have a pleasing 5 fragrance. For those compositions which are intended to be used in a domestic environment, the fragrance constituent, as well as the other ingredients used in making up compositions of the invention should be cosmetically acceptable, i.e., feature low toxicity or no toxicity, hypoallergenic character, etc. The fragrance constituent may be included in any effective amount. Most desirably however the fragrance constituent is chosen to 10 be compatible with the Marseilles soap and to imitate the fragrance provided by the Marseilles soap itself.

According to certain preferred embodiments of the invention, one or more opacifiers are necessarily included in the composition as such are particularly attractive from a consumer standpoint. Exemplary opacifiers include for example those based on 15 acrylic polymers, including styrene acrylic polymers such as are available within the Acusol® line of products from Rohm & Haas. Further opacifiers include those based on higher molecular weight polyethylene glycols such as are available within the Renopal® line of products from Goldschmidt Corp., as well as those based on alkylene glycol stearates such as are available in the Cithrol® like of products from Croda Corp.

When included, the one or more further optional constituents which are directed to improving the aesthetic or functional features of the inventive compositions are present in the compositions of the present invention in any amount which is effective providing a desired aesthetic or functional feature. The total amount of these optional compositions present in the inventive compositions do not exceed about 10%wt., preferably do not 20 exceed 2%wt., and most preferably do not exceed 1%wt.

As is noted above, the compositions according to the invention are largely aqueous in nature. Water is added to order to provide to 100% by weight of the compositions of the invention. The water may be tap water, but is preferably distilled and is most preferably deionized water. If the water is tap water, it is preferably 25 substantially free of any undesirable impurities such as organics or inorganics, especially minerals salts which are present in hard water which may thus undesirably interfere with

the operation of the constituents present in the aqueous compositions according to the invention.

The compositions are desirably at a neutral or alkaline pH, but desirably are at a pH of at least 7. Most desirably the inventive compositions are at a pH of about 8 to 5 about 12.

In preferred embodiments, the inventive compositions exhibit excellent stability when subjected to storage at room temperature, storage under elevated temperatures (105°F, 120°F). In addition, especially preferred embodiments of the inventive compositions also exhibit excellent stability when subjected to successive free-thaw 10 cycles.

The stability of an inventive composition to storage under room temperature (approx. 20°C, 68°F) can be evaluated by visual observation, particularly by evaluating the homogeneity of the composition, essentially the lack of two or more separate phases or of any precipitation, of the compositions. These evaluations are preferably made at 15 each 24 hour interval in a seven day period following the production of the composition. Ideally if the compositions exhibit the lack of any precipitated materials at the bottom of the container, then the composition is considered acceptable.

The stability of an inventive composition to storage under elevated temperatures (approx. 50°C, 122°F) can be evaluated by subjecting the composition to the elevated 20 temperature for 24 hour intervals, thereafter removing the heated composition and then allowing it to cool to room temperature and then visually evaluating the homogeneity of the compositions as noted above. Subsequently the composition is resubjected to the elevated temperature for 24 hour intervals, and again removed, allowed to cool to room temperature and then visually reevaluated. This process of heating, cooling and evaluation 25 are desirably repeated for 7 days. Again, the compositions are considered acceptable if they exhibit the lack of any precipitated materials at the bottom of the container when evaluated over this 7 day period.

In addition to excellent storage stability under room temperature and under elevated temperature conditions preferred embodiments of the inventive compositions 30 also exhibit excellent stability when subjected to successive free-thaw cycles. Stability to successive free-thaw cycles can be evaluated by forming a composition and thereafter

freezing it to a solid mass, and thereafter permit it to thaw to 5°C. The thawed compositions may be manually shaken before evaluating their appearance. The composition may then be refrozen, and rethawed according to the same protocol, and reevaluated, and this cycle repeated a third time as well. The compositions are
5 considered acceptable if they exhibit the lack of any precipitated materials at the bottom of the container when evaluated after three free-thaw cycles.

It is a further object of the invention to provide a process for the cleaning of hard surfaces which process comprises the step of: providing a composition as outlined above, and applying an effective amount of the said composition requiring treatment. The
10 inventive compositions are desirably provided as a ready-to-use product which may be directly applied to a hard surface. By way of example, hard surfaces include surfaces composed of refractory materials such as: glazed and unglazed tile, brick, porcelain, ceramics as well as stone including marble, granite, and other stones surfaces; glass; metals; plastics e.g. polyester, vinyl; fiberglass, Formica®, Corian® and other hard
15 surfaces known to the industry. Hard surfaces which are to be particularly denoted are lavatory fixtures such as shower stalls, bathtubs and bathing appliances (racks, curtains, shower doors, shower bars) toilets, bidets, wall and flooring surfaces especially those which include refractory materials and the like. Further hard surfaces which are to be denoted are those associated with kitchen environments and other environments
20 associated with food preparation, including cabinets and countertop surfaces as well as walls and floor surfaces especially those which include refractory materials, plastics, Formica®, Corian® and stone. Such hard surfaces described above are to be understood as being recited by way of illustration and not be way of limitation.

In preferred embodiments, the compositions are readily pumpable using a
25 manually operable trigger spray apparatus and are desirably provided as a ready to use product in a container package which comprises a manually operable trigger spray apparatus and a non-pressurized reservoir or bottle for containing the inventive compositions. In use, the consumer generally applies an effective amount of the composition and within a few moments thereafter, wipes off the treated area with a rag, towel, brush or sponge, usually a disposable paper towel or sponge. In certain
30 applications, however, especially where undesirable stain deposits are heavy, the

composition according to the invention may be left on the stained area until it has effectively loosened the stain deposits after which it may then be wiped off, rinsed off, or otherwise removed. For particularly heavy deposits of such undesired stains, multiple applications may also be used.

5 The inventive compositions may be produced by any of a number of known art techniques. Most simply the constituents may be added, under stirring to a large aliquot of the water used to produce the formulation until all of the constituents are added with the final amount of water added last. Alternately a large aliquot of the water is added to a mixing vessel provided with an agitator, and under agitation the following constituents
10 are added in the following order: organic solvent, Marseilles soap, surfactants, source of potassium ions, optional constituents (e.g., preservative, opacifier, fragrance, coloring agents) and finally any remaining water needed to provide the remaining 100%wt of the composition. All or some of the individual constituents may be preheated in order to facilitate their mixing with the water, and the water may also be heated to an elevated
15 temperature, but usually not heated in excess of about 90°C, and preferably not in excess of about 40°C.

A first preferred process for the manufacture of the inventive compositions contemplates adding to a suitable mixing vessel containing the total amount of water (preferably "soft water") which is heated to 20°C-25°C the organic solvent(s), followed
20 by the Marseilles soap which is stirred under moderate agitation using a conventional electrically driven laboratory agitator, and stirring is continued until the soap is melted and a homogenous mixture is formed. Subsequently under continued stirring is added the nonionic surfactant, then the source of potassium ions, and stirring is permitted to continue until the composition clarifies. Thereafter the remaining constituents may be
25 added in any order, except for the opacifier which, when present, is provided in the last step.

A second preferred process for the manufacture of the inventive compositions contemplates the following steps. To a suitable mixing vessel is supplied the total amount of "soft water" which heated to 40°C, to which is added the Marseilles soap
30 which is stirred under moderate agitation using a conventional electrically driven laboratory agitator, and stirring at 40°C is continued until the soap is melted and a

homogenous mixture is formed. Heating is discontinued, and thereafter the source of potassium ions is added to the solution, and stirring continued until the composition is homogenous and the composition clarifies. Subsequently under continuous stirring are added in order: surfactant(s), organic solvent(s), and when present, the remaining constituents, e.g., preservative, fragrance, and lastly the opacifier if included.

5 The following examples below illustrate exemplary formulations as well as preferred embodiments of the invention. It is to be understood that these examples are provided by way of illustration only and that further useful formulations falling within the scope of the present invention and the claims may be readily produced by one skilled 10 in the art without deviating from the scope and spirit of the invention.

Examples

Certain embodiments of the invention, including preferred embodiments of the invention are described amongst the following example formulations. Also provided are 15 certain comparative formulations. The compositions presented in the example formulations as well as the comparative formulations were produced in accordance with either the first preferred process, or the second preferred process for the manufacture of the inventive compositions outlined above, the manner of their manufacture is not critical to the properties of the inventive compositions.

Table 1

	Ex.1 (%wt)	Ex.2 (%wt)	Ex.3 (%wt)	Ex.4 (%wt)	Ex.5 (%wt)	Comp.A (%wt.)	Comp.B (%wt.)	Comp.C (%wt.)	Comp.D (%wt.)	Comp.E (%wt.)
Marseille Soap	1.15	1.15	1.15	3.0	1.15	1.0	1.15	1.15	1.0	1.15
di(propylene glycol) n-butyl ether	1.4	1.4	--	--	1.4	2.5	--	--	2.0	2.0
isopropanol	--	--	--	1.5	--	--	3.75	2.0	--	--
propylene glycol	--	--	--	--	--	--	1.0	--	--	--
C9-C11 alkyl/ethoxylate, 6EO	4.5	5.0	5.0	3.0	4.5	4.0	--	--	3.0	1.0
C8-C11 alkyl/ethoxylate, 6EO	--	--	--	--	--	--	--	4.0	--	--
ethoxylated fatty alcohols/quaternary ammonium chlorides	--	--	--	--	--	--	--	--	1.5	--
linear alkylbenzene sulfonate	--	--	--	--	--	--	--	--	--	5.25
TEA-alkylbenzene sulfonate	--	--	--	--	--	--	--	--	--	1.0
sodium cumene sulfonate	--	--	--	--	--	--	1.0	--	--	--
potassium tripolyphosphate, anhydrous	0.9	1.0	1.0	--	--	--	--	--	--	--
tetrapotassium pyrophosphate	--	--	--	--	0.9	--	--	--	--	--
potassium hydroxide	--	--	--	3.0	--	--	--	--	--	--
sodium hydroxide	--	--	--	--	--	--	--	0.15	--	--
styrene acrylic polymer	0.125	0.125	0.125	--	0.125	--	--	--	0.125	--
preservative composition	0.3	0.3	0.3	--	0.3	0.3	0.3	--	--	0.3
fragrance	0.2	0.2	0.2	--	0.2	0.2	0.25	--	--	0.2
monoethanolamine	--	--	--	--	--	--	--	0.75	--	--
triethanolamine	--	--	--	--	--	0.5	0.5	--	--	--
tetrasodium ethylene diamine	--	--	--	--	--	--	--	0.04	--	--
tetraacetic acid	--	--	--	--	--	--	--	0.165	--	--
citric acid	--	--	--	--	--	--	--	0.005	--	--
polydimethylsiloxane emulsion	--	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
deionized water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.

The constituents used to produce the formulations described on Table 1 are described on the following Table 2, which lists the commercial source of the named chemical compound.

Table 2	
Marseille Soap	Marseille Soap (100%wt. actives) ex. Chimotechnique/Nouvelle Savonnerie Francaise
di(propylene glycol) n-butyl ether	Dowanol® DPnB (98%wt. actives) ex. Dow Chemical Corp.
isopropanol	isopropanol (100%wt. actives)
propylene glycol	propylene glycol (100%wt. actives)
C9-C11 alkylethoxylate, 6EO	Neodol® 91-6 (100%wt. actives) ex. Shell
C8-C11 alkylethoxylate, 6EO	Neodol® 91-8 (100%wt. actives) ex. Shell
ethoxylated fatty alcohols/quaternary ammonium chlorides	Rewoquat® CQ 100 (100%wt. actives) ex. Degussa Corp.
linear alkylbenzene sulfonate	Bio-Soft® D-40 (40%wt. actives) ex. Stepan Co.
TEA-alkylbenzene sulfonate	Bio-Soft® N-300 (60%wt. actives) ex. Stepan Co.
sodium cumene sulfonate	Stepanate® SCS (40%wt. actives) ex. Stepan co.
potassium tripolyphosphate, anhydrous	anhydrous potassium tripolyphosphate (100%wt. actives) ex. Astaris
tetrapotassium pyrophosphate	tetrapotassium pyrophosphate (100%wt. actives) ex. Astaris
potassium hydroxide	potassium hydroxide (80%wt. actives)
sodium hydroxide	sodium hydroxide (50%wt. actives) ex. VWR
styrene acrylic polymer	Acusol® OP 305 (40%wt. actives) ex. Rohm & Haas
preservative composition	1,3-dihydroxymethyl-5,5-dimethylhydantoin and 3-iodo-2-propynyl butyl carbamate commercially sold as Dantogard® Plus (70%wt. actives) ex. Lonza Corp.
fragrance	So. Marseille 24 (proprietary composition)
monoethanolamine	monoethanolamine (99%wt. actives) ex. Dow Chemical Corp.
triethanolamine	triethanolamine (99%wt. actives) ex. Dow Chemical Corp.
tetrasodium ethylene diamine tetraacetic acid	tetrasodium ethylene diamine tetraacetic acid (100%wt. actives) ex. AKZO-Nobel
citric acid	citric acid (100%wt. actives) ex. ADM Corp.
polydimethylsiloxane emulsion	Dow Corning 1520® (6%wt. actives) ex. Dow Chemical Corp.
deionized water	deionized water, or "soft water"

The physical properties of several compositions described in Table 1 were evaluated in accordance with one or more of the following protocols.

In addition to excellent storage stability under room temperature and under elevated temperature conditions preferred embodiments of the of the invention also 5 exhibited excellent stability when subjected to successive freeze-thaw cycles, which was evaluated according to the following general protocols:

Separate aliquots of each of the Example compositions, as well as separate aliquots of certain of the Comparative compositions described on Table 1 were subjected to stability testing at room temperature (approx. 20°C), as well as under elevated 10 temperature conditions, (approx. 50°C) and to three successive freeze thaw cycles in accordance with the protocol recited previously. For the evaluations at room temperature, visual evaluations were made at 24 hours, 48 hours and 1 week after the initiation of the test; none of the Example compositions were observed to exhibit any precipitated materials at the bottom of the container. For the evaluations at elevated 15 temperature conditions, visual evaluations were made at 24 hours, 48 hours and 1 week after the initiation of the test; none of the Example compositions were observed to exhibit any precipitated materials at the bottom of the container. Similarly for evaluations subsequent to three successive freeze-thaw cycles, visual evaluations were made and none of the Example compositions were observed to exhibit any precipitated materials at 20 the bottom of the container.

Each of the Comparative compositions described on Table 1 were formed in the same manner as the Example compositions, and the following observations are noted. The composition according to Comp. A did not include a source of potassium ions, and after 7 days of testing at elevated temperature conditions, (approx. 50°C), a significant 25 amount of precipitate was observed at the bottom of the container in which it was tested. The composition according to Comp. B, subsequent to 7 days of testing at elevated temperature conditions, (approx. 50°C), a significant amount of precipitate was observed at the bottom of the container in which it was tested. Similarly, for the composition according to Comp. C, subsequent to 7 days of testing at elevated temperature conditions, 30 (approx. 50°C), a significant amount of precipitate was observed at the bottom of the container in which it was tested. The composition of Comp. D failed to form a

homogenous mixture, and instead formed a gelatinous body which could not be remixed. The composition according to Comp. E did not include a source of potassium ions, and further, after exhibited precipitate after 7 days of storage at a low temperature (4.5°C, 40°F).

5 As described above, each of the Comparative compositions exhibited precipitation of material during one or more of the stability tests at room temperature, and/or elevated temperature and/or subsequent to three successive freeze-thaw cycles, or could not be formed into homogenous liquid mixtures containing a source of potassium ions.

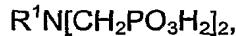
10 As can be seen from the foregoing the compositions of the invention were superior to the comparative compositions.

While the invention is susceptible of various modifications and alternative forms, it is to be understood that specific embodiments thereof have been shown by way of examples which are not intended to limit the invention to the particular forms disclosed; on the contrary the intention is to cover all modifications, equivalents and alternatives 15 falling within the scope and spirit of the invention as expressed in the appended claims.

Claims:

1. An aqueous hard surface cleaning composition which comprises (preferably 5 consists essentially of):
 - Marseille soap;
 - a surfactant constituent, desirably an anionic surfactant, a nonionic surfactant or mixtures thereof, but most desirably solely a nonionic surfactant;
 - a source of potassium ions;
 - 10 optionally but desirably an organic solvent constituent, desirably one or more glycol ethers;
 - optionally but desirably a preservative constituent;
 - optionally one or more further constituents which are directed to improving the aesthetic or functional features of the inventive compositions;
 - 15 the balance being water.
2. The composition according to claim 1 wherein the Marseilles soap comprises at least 72%wt. pure soap, contains not more than 0.1%wt. free soda, contains not more than 0.4%wt. sodium chloride, and contains not more than 0.5%wt. glycerol.
- 20 3. The composition according to claim 1 or 2 wherein the Marseilles soap comprises 0.2%wt. to about 3.0% by weight of the composition.
4. The composition according to claim 1 wherein the source of potassium ions is an 25 inorganic potassium salt.
5. The composition according to claim 4 wherein the source of potassium ions is selected from: alkali metal pyrophosphate, an alkali metal polyphosphates and phosphonic acids.

6. The composition according to claim 5 wherein the source of potassium ions is a phosphonic acid which may be represented by one of the following general formula:



wherein R^1 may represent a $-(C_1-C_6)\text{alkylene}-N-[CH_2PO_3H_2]_2$ group or may represent a
5 third $-(CH_2PO_2H_2)$ group,

or,



wherein R^2 is a C_1-C_6 alkyl group.

10 7. The composition according to claim 5 wherein the source of potassium ions are selected from: potassium salts of a low molecular weight phosphonopolycarboxylic acid having about 2 – 4 carboxylic acid moieties and about 1 – 3 phosphonic acid groups, potassium salts of alkylene phosphonic acids, and phosphorous acid (H_3PO_3).

15 8. The composition according to claim 1 wherein the source of potassium ions are selected from potassium carbonates, potassium phosphates, potassium polyphosphates, and potassium pyrophosphates.

9. The composition according to claim 9 wherein the source of potassium ions are
20 selected from: potassium tripolyphosphate, tetrapotassium pyrophosphate and potassium hydroxide.

10. The composition according to claim 1 wherein the source of potassium ions is present in sufficient amounts such that the final concentration of available potassium ions
25 are from about 50 ppm to about 20,000 ppm,

11. The composition according to claim 10 wherein the source of potassium ions is present in amounts of from about 2000 ppm to about 6000 ppm.

30 12. The composition according to claim 1 wherein the surfactant constituent comprises a nonionic surfactant based on a linear primary alcohol ethoxylate wherein the

alkyl portion is a C₈ to C₁₂, alkyl group, and having an average of between about 6 to about 8 moles of ethoxylation.

13. The composition according to claim 1 wherein the surfactant constituent consists
5 solely of a nonionic surfactant based on a linear primary alcohol ethoxylate wherein the alkyl portion is a C₈ to C₁₂, alkyl group, and having an average of between about 6 to about 8 moles of ethoxylation.
14. The composition according to claim 1 wherein the surfactant constituent is
10 present in amount of from about 0.01%wt. to about 50%wt.
15. The composition according to claim 1 wherein the organic solvent constituent is selected from one or more alcohols, glycols, acetates, ether acetates and glycol ethers.
16. The composition according to claim 15 wherein the organic solvent constituent is
15 a glycol ether.
17. The composition according to claim 1 wherein the organic solvent constituent is present in an amount of from about 0.01%wt. to about 20%wt.
18. The composition according to claim 1 which contains a preservative constituent.
19. The composition according to claim 1 which contains a fragrancing agent.
20. 20. The composition according to claim 1 which, when subjected to storage under room temperature (approx. 20°C , 68°F) conditions exhibits the lack of any precipitated materials at the bottom of the container after 7 days of storage under such conditions.
21. The composition according to claim 1 which, when subjected to storage under
30 elevated temperatures (approx. 50°C, 122°F) exhibits the lack of any precipitated

materials at the bottom of the container when evaluated after 7 days of storage under such conditions.

22. The composition according to claim 1 which, when subjected to three successive
5 free-thaw cycles exhibit the lack of any precipitated materials at the bottom of the
container when evaluated after said three free-thaw cycles.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/002180

A. CLASSIFICATION OF SUBJECT MATTER				
IPC 7 C11D10/04 C11D3/20 C11D3/36 C11D3/06 C11D3/02				
<p>According to International Patent Classification (IPC) or to both national classification and IPC</p>				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols)				
IPC 7 C11D				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)				
EPO-Internal, WPI Data, PAJ				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category ^o	Citation of document, with indication, where appropriate, of the relevant passages			Relevant to claim No.
X	DE 663 153 C (BOEHME FETTCHEMIE GES M B H) 30 July 1938 (1938-07-30) claims; example 5			1,2,10, 11,14, 20-22
X	EP 0 522 604 A (COLGATE PALMOLIVE CO) 13 January 1993 (1993-01-13) page 2, lines 48-57 page 3, lines 35-47 page 5, lines 41-50 page 9, lines 26-48 claims 1-4; examples 1-3			1-22
X	EP 0 649 898 A (CLOROX CO) 26 April 1995 (1995-04-26) page 3, lines 48-55 examples i-vi			1-22
				-/-
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		<input checked="" type="checkbox"/> Patent family members are listed in annex.		
<p>^o Special categories of cited documents :</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*&* document member of the same patent family</p>				
Date of the actual completion of the international search		Date of mailing of the international search report		
19 August 2004		30/08/2004		
Name and mailing address of the ISA		Authorized officer		
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Bertran Nadal, J		

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/002180

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 752 411 A (PETON NICOLE ET AL) 21 June 1988 (1988-06-21) column 2, lines 44-66 column 3, lines 18-24 examples 1-3 -----	1-22
X	WO 98/23723 A (HENKEL KGAA) 4 June 1998 (1998-06-04) page 3, paragraph 2 – page 4, paragraph 1 examples -----	1-22
A	FR 872 219 A (LETALLEC E J) 2 June 1942 (1942-06-02) page 1, lines 1-14 examples -----	1-22
A	US 4 058 473 A (CANTER CARL ROBERT) 15 November 1977 (1977-11-15) column 1, lines 54-68 claim 1 -----	1-22
A	US 4 507 219 A (HUGHES LARRY J) 26 March 1985 (1985-03-26) column 3, lines 8-40 column 5, line 59 – column 6, line 10 examples -----	1-22

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/GB2004/002180

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
DE 663153	C	30-07-1938	AT BE FR GB US	132006 B 374774 A 725111 A 361565 A 2046242 A	25-02-1933 09-05-1932 26-11-1931 30-06-1936
EP 0522604	A	13-01-1993	AU AU CA EP FI GR IE NO NZ PT US	650121 B2 1493892 A 2066289 A1 0522604 A2 921744 A 92100157 A 921275 A1 921479 A 242381 A 100396 A 5395547 A	09-06-1994 14-01-1993 11-01-1993 13-01-1993 11-01-1993 24-05-1993 13-01-1993 11-01-1993 24-02-1995 31-08-1993 07-03-1995
EP 0649898	A	26-04-1995	CA EP US US	2134062 A1 0649898 A2 5529711 A 5827810 A	23-04-1995 26-04-1995 25-06-1996 27-10-1998
US 4752411	A	21-06-1988	FR AR AU AU CA DE DK EP FI JP JP JP KR NO OA	2564853 A1 240474 A1 581226 B2 4301485 A 1271681 A1 3564699 D1 233985 A ,B, 0165885 A1 852104 A ,B, 1781098 C 4071439 B 60258299 A 9206029 B1 852085 A ,B, 8037 A	29-11-1985 30-04-1990 16-02-1989 05-12-1985 17-07-1990 06-10-1988 29-11-1985 27-12-1985 29-11-1985 13-08-1993 13-11-1992 20-12-1985 27-07-1992 29-11-1985 31-01-1987
WO 9823723	A	04-06-1998	DE AT DE WO EP	19649102 A1 201901 T 59703741 D1 9823723 A1 0944712 A1	28-05-1998 15-06-2001 12-07-2001 04-06-1998 29-09-1999
FR 872219	A	02-06-1942	NONE		
US 4058473	A	15-11-1977	AT AT BE CA CH DE DK FR GB IT JP	362852 B 436477 A 855891 A1 1081576 A1 627781 A5 2728356 A1 279677 A ,B 2355910 A1 1538845 A 1083546 B 1245302 C	25-06-1981 15-11-1980 20-12-1977 15-07-1980 29-01-1982 29-12-1977 25-12-1977 20-01-1978 24-01-1979 21-05-1985 25-12-1984

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/002180

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
US 4058473	A		JP 53000209 A	05-01-1978
			JP 58033920 B	22-07-1983
			NL 7706574 A	28-12-1977
			NO 772182 A ,B,	28-12-1977
			SE 433089 B	07-05-1984
			SE 7707342 A	25-12-1977
US 4507219	A	26-03-1985	AT 34181 T	15-05-1988
			AU 561794 B2	14-05-1987
			AU 3182784 A	14-02-1985
			CA 1231027 A1	05-01-1988
			DE 3471115 D1	16-06-1988
			EP 0151678 A1	21-08-1985
			GB 2144764 A ,B	13-03-1985
			GR 80005 A1	30-10-1984
			HK 75090 A	28-09-1990
			IE 57605 B1	27-01-1993
			JP 5059957 B	01-09-1993
			KR 9106071 B1	12-08-1991
			MX 161032 A	11-07-1990
			SG 43290 G	17-08-1990
			JP 1857922 C	27-07-1994
			JP 60106892 A	12-06-1985